Co, Fe, Mo BASED OIL SOLUBLE DISPERSED CATALYST FOR HYDROCRACKING OF HEAVY OIL

BY

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Dedicated to my Parents almighty Allah blesses them

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND NOMENCLATURE

VGO	:	Vacuum Gas Oil
TGA	:	Thermal Gravimetric Analysis
LPG	:	Liquefied Petroleum Gas
LCO	:	Light Cycle Oil
HCO	:	Heavy Cycle Oil
C/O	:	Catalyst to Oil ratio
SEM	:	Scanning Electron Microscopy
FTIR	:	Fourier Transform Infrared
T	:	Reaction temperature
T_o	:	Average temperature of the experiments
R	:	Universal gas constant

ABSTRACT

Full Name : Emadaldeen Sami Bdwi Babiker

Thesis Title : Co, Fe, Mo Based Oil Soluble Dispersed Catalyst For Hydrocracking Of VGO

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This study deals with the promotional effects of dispersed catalysts on hydrocracking of vacuum gas oil (VGO). The influence of oil soluble Mo, Fe and Co based materials is investigated with and without the presence of a commercial first-stage hydrocracking W-Ni/Al_2O_3-SiO_2 catalyst. The experiments are conducted in a batch autoclave reactor (at 8 MPa and 420 °C). It is showed that the dispersed metal catalysts enhances the hydrogenation activity and reduced coke formation. Among the three catalysts, Co and Mo based catalysts show lower coke formation than the Fe catalyst. It is observed that the addition of 500 ppm of Co/Mo decreased the coke to 0.9 wt % from 2.5 wt % observed during the thermal cracking. The addition of a dispersed catalyst together with the supported catalyst show similar decrease in coke formation. The presence of dispersed catalyst along with the supported catalyst also enhances the yield of naphtha. A kinetic model is developed based on the experimental data obtained from tests using dispersed and supported catalysts. The model incorporates coke formation along with the conversion of VGO to distillate, naphtha, and gaseous hydrocarbons. The activation energy of VGO hydrocracking forming distillate requires the least activation energy (1.5 kcal/mol) as compared to the other competing reactions. Hence it is concluded that VGO is most likely cracked to form distillate then distillate is cracked to form naphtha, and naphtha is cracked to gases.

ملخص الرسالة

الاسم الكامل: عماد الدين سامي بدوي بابكر

عنوان الرسالة: التكسير الهيدروجيني للزيت الثقيل عن طريق المحفزات المشتته القابلة للذوبان في الزيت كال(Co,Fe,Mo)

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: يناير 2017

تتناول الدراسة الحالية الآثار الإيجابية للمحفزات المشتتة القابلة للذوبان في الزيت وأثرها الإيجابي في التكسير الحفزي الهيدروجيني لل (VGO). في هذا السياق تمت دراسة كل من ال(Mo,Fe and Co). وعلى هذا الأساس تم إجراء التجارب في مفاعل من النوع (batch autoclave reactor) عند ضغط 4 ميجا باسكال ودرجة حرارة 420 درجة مئوية عند وجود وعدم وجو حفاز مدعم صلب تجاري بالصيغة (W-Ni/Al2O3-SiO2). تم ملاحظة أن المحفزات المشتته تقوم بتحسين تفاعلات الهدرجة وبالتالي تقوم بتقليل كمية الفحم المتكونة. أقل كمية من الفحم تمت ملاحظتها عند إستخدام 500 ppm من المحفز المشتت. من بين الثلاثة أنواع من المحفزات المشتتة المستخدمة تمت ملاحظة أن المحفزات المكونة من (Co/Mo) تؤدي الى ظهور فحم أقل من تلك التي تستخدم ال(Fe). كما تم ملاحظة أن المحفزات المشتتة المكونة من ال(Co/Fe) عند تركيز 500 ppm تؤدي الى إنقاص النسبة الوزنية للفحم المتكون من 2.5% الى 0.9% مقارنة بالكتسير الحراري دون استخدام المحفز. إضافة المحفزات المشتتة للمحفز الصلب قامت أيضا بتقليل كمية الفحم المتكونة وزيادة نسبة النافثا المتكونة وتقليل نسبة ال(VGO) غير المتكسرة. تم تطوير نموذج لحركية التفاعلات بناء على تجارب تم إجرائها في نفس المفاعل المذكور اعلاه في المدى الحراري من 390 إلى 450 درجة مئوية. للنمذجة تم إستخدام ال(Power law model) كما تم إستخدام برنامج ال(MATLAB) لايجاد المعاملات للنموذج المستخدم.

CHAPTER 1

INTRODUCTION

1.1 Background

Heavy oils are the high density viscous petroleum feedstocks. Generally, the petroleum with an API gravity less than 20° are considered as heavy oil [1]. Over the years, the demand for lighter petroleum products is rising. It is expected to increase further, as shown in Figure 1.1.

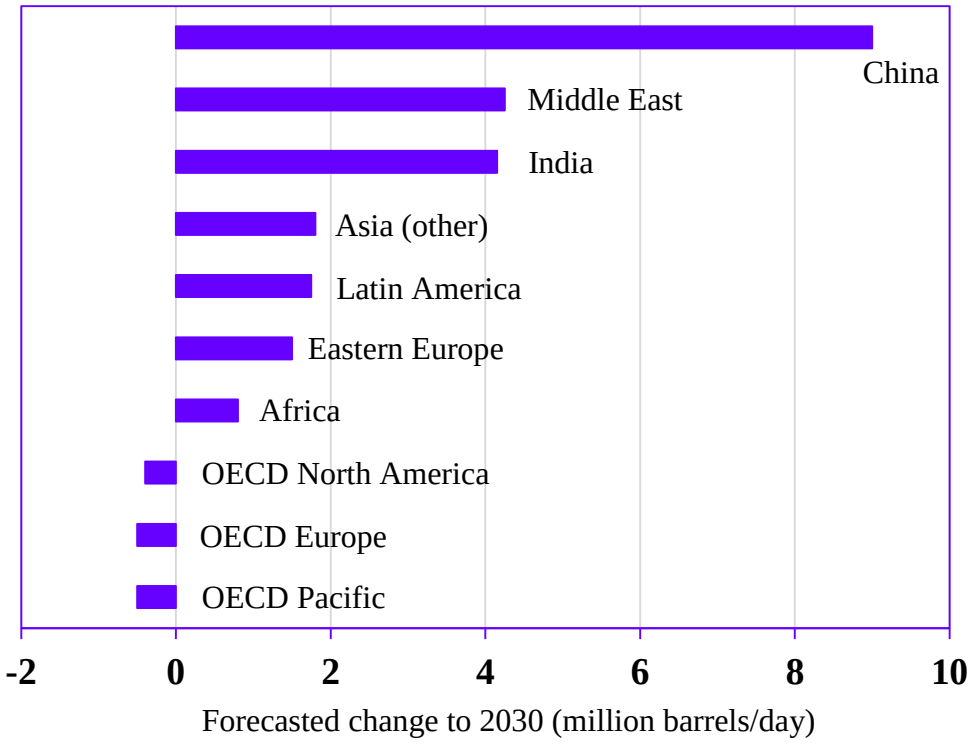


Figure 1.1: Expected change in crude oil demand in 2030 (source, EIA)

On the other hand, the supplies of the conventional light crude oils are depleting. In addition, the demand for low value product like fuel oil, bitumen, VGO are decreasing due to the

environmental issues related to combustions of these heavy oils [1]. The estimated total reserves for bitumen and heavy oil is 5.6 trillion barrels as compared to the remaining conventional crude oil reserves of 1.02 trillion barrels [2]. Therefore, there is a growing need to develop more efficient technologies in order to process heavy oils to produce lighter products with minimum environmental impacts. Hydrocracking of heavy oils is one of the most commonly used processes for heavy oil upgrading.

1.2 History of hydrocracking

The hydrocracking technology was first developed in Germany in 1915 to provide higher value liquid fuels from coal. The first commercialized plant started operation back in 1927 at Leuna, Germany. Other countries, like Britain and France also made efforts to develop similar technologies to convert coal to liquid fuel [3]. During the similar period (1925 -1930), the Standard Oil of New Jersey, USA, cooperated with I.G. Farben industries of Germany to develop hydrocracking technology for upgrading of heavy petroleum oils. However, this process was found to be very expensive due to its high pressure (20 – 30 MPa) and temperatures (>375 °C).

In the years between 1960 and 1970, the hydrocracking process showed a remarkable development in the United States. Since then, the hydrocracking technology became a well-known commercial process [3]. By the year of 2001, total 155 hydrocracking units have been established around the world which process over 4 million barrels oils per day.

1.3 Fixed bed versus slurry phase hydrocracking

There are two types of well-known technologies available for hydrocracking of heavy oil, (i) fixed bed technology and (ii) slurry processes. The slurry process can handle high impurity crude, which is common in heavy oils [3,4]. Another important advantage of slurry process is the intimate contact between the catalyst and the feed due to the movement of the smaller size catalysts inside the reactor. The available surface area of the slurry catalyst is also higher because of the well mixed feed and catalyst, which minimizes the mass transfer limitations. The slurry process also provide with the option of catalyst regeneration/refill, as it allows withdrawing from and re-entering the catalyst into the reactor. This way, the process can be controlled to achieve desired products [6].

1.4 Chemistry of hydrocracking

Hydrocracking involves two major reactions: (i) cracking of the heavy hydrocarbon molecules of the heavy feed into smaller hydrocarbon intermediates, and (ii) hydrogenation of the cracked intermediates into stable lighter products. Further, he cracking reactions are endothermic, while the hydrogenation reactions are exothermic. Therfore, the overall heat of reactions will be determined by the degree of cracking and hydrogenation reactions.

For example, at elaveted temperature (above 375 °C), in presence of hydrogen and a suitable catalyst, $C_{22}H_{46}$ can be broken into $C_{16}H_{34}$ and C_6H_{14}, as shown the following reaction:

$$C_{22}H_{46} + H_2 \rightarrow C_{16}H_{34} + C_6H_{14}$$

The other type of reactions also occur in hydrocracking process which improves oil properties these reactions are hydrodesulfurization (HDS), hydrodemetalation (HDM) and

hydrodenitrification (HDN). These reactions decrease sulfur, metal and nitrogen from the oil products, which are undesired in the product specifications [7].

The above reactions are just an example. In reality, the heavy oil consists of many components. Therefore, in addition to the hydrocracking and hydrogenation reactions there are other types of reactions that might take place. Therefore, the hydrocracking reactions are much complex. One way to study the hydrocracking reaction is to study the reactions as groups [8]. One can consider the following as main reactions that involve in a typical heavy oil hydrocracking process:

i. Hydrogenation of aromatics and olefins.
ii. Hydrogenation of polyaromatics.
iii. Hydrodealkylation.
iv. Hydrodecycliation of polyaromatic/naphthenic complexes.
v. Isomerization of paraffin and naphthenes.
vi. Cracking of iso-paraffin, alkyaphthenes, and alkylaromatics (hydrocrackig).
vii. Coking (which will lead to the deactivation of the catalyst).

1.5 The role of catalyst

Regarding the catalysts, both the fixed and slurry processes require dual (cracking and hydrogenation) functional supported metal catalysts. The acidic function, provided by the support material, and is responsible for cracking of the heavy hydrocarbon molecules. The metal function, facilitates the dehydrogenation/hydrogenation reactions. In addition, there are some desirable side reactions such as hydroisomerization and dehydrocyclization enhanced by both the metallic and acidic functions [6,7]. One of the important issues related to the hydrocracking is

the catalyst deactivation by coke formation. During the cracking process coke is produced and is deposited on the catalyst blocking its active sites and deactivating them quickly [4]. Application of dispersed catalysts has been considered as an interesting alternative to minimize the coke problems. Usually, the transition metals such as Co, Mo, W and Fe are good candidates as a dispersed catalyst.

The dispersed catalysts are effective in slowing down the deactivation rate of the supported catalyst because of their hydrogenation activity on the smaller crystal size [8,9]. The dispersed catalysts also have no diffusion problem, which allows easy access of the large hydrocarbon molecules to the active sites, and thus reduce the coke formation by hydrogenating the cracked intermediate free radicals [5,10]. Metal sulfides, which are formed by the reaction between metal precursors and sulfur compounds in the feedstock or additional sulfur sources, have been proved to be the active species in hydrocracking processes [13].

1.6 Objective

Based on the above discussion, this research is focused on the development of oil soluble dispersed catalyst(s) suitable for slurry phase heavy oil hydrocracking. In catalyst formulation, Co, Mo and Fe based organic precursors have been employed as main active components. The catalysts are evaluated using heavy vacuum gas oil as a feedstock.

The following are identified as the specific objectives of this study:

i. Slurry phase hydrocracking of VGO using oil soluble monometallic dispersed catalysts (Co, Mo, Fe) as standalone catalysts.

ii. Slurry phase hydrocracking of VGO using oil soluble monometallic dispersed catalysts (Co, Mo, Fe) as an additive along with a solid Ni-W/Al_2O_3-SiO_2 hydrocracking catalyst.

iii. Characterization of the catalysts to determine metal dispersion and in-situ catalyst sulphiding using SEM and FTIR techniques, respectively.

iv. The kinetic modeling of the slurry phase hydrocracking of VGO is also carried. A five lumped kinetics model is formulated based on the product distributions. The kinetics parameters are estimated by least-squares fittings of the model equation using experimental data implemented in MATLAB. The estimated parameters are evaluated based on their physical significances and various statistical indicators.

CHAPTER 2

LITERATURE REVIEW

2.1 Hydrocracking

Hydrocracking is the process where the heavy oil or the residuum is cracked then hydrogenated into more valuable lower molecular weight products. As the nature of the process is to perform two functions so the catalyst has to be bifunctional. The acid part of the catalyst is to enhance the cracking reactions and the metallic part to enhance the hydrogenation reactions. The purpose of hydrogenation reaction is not just to saturate the unsaturated bond resulted from the cracking reactions but also to enhance the oil properties by removing the impurities such as sulfur. The sulfur containing heteroatoms firs cracks to liberate sulfur, which reacts with hydrogen and transferred to hydrogen sulfide. By similar fashion, the other impurities such as nitrogen, oxygen and metals can be removed [9].

2.1.1 The role of hydrocracking in refinery

Hydrocracking is indispensible process in many refineries. As shown in Figure (2.1) the role of the hydrocracking process is mainly after distillation processes. The main use of the catalytic hydrocracking unit in the refinery is to produce a low sulphur percentage of kerosene and diesel[9] . At a recent time, hydrocracking process used for other purposes such as removing the wax using catalytic dewaxing process. In addition, it can be used to remove aromatic using the hydrogen to saturate the unsaturated bonds in aromatics.

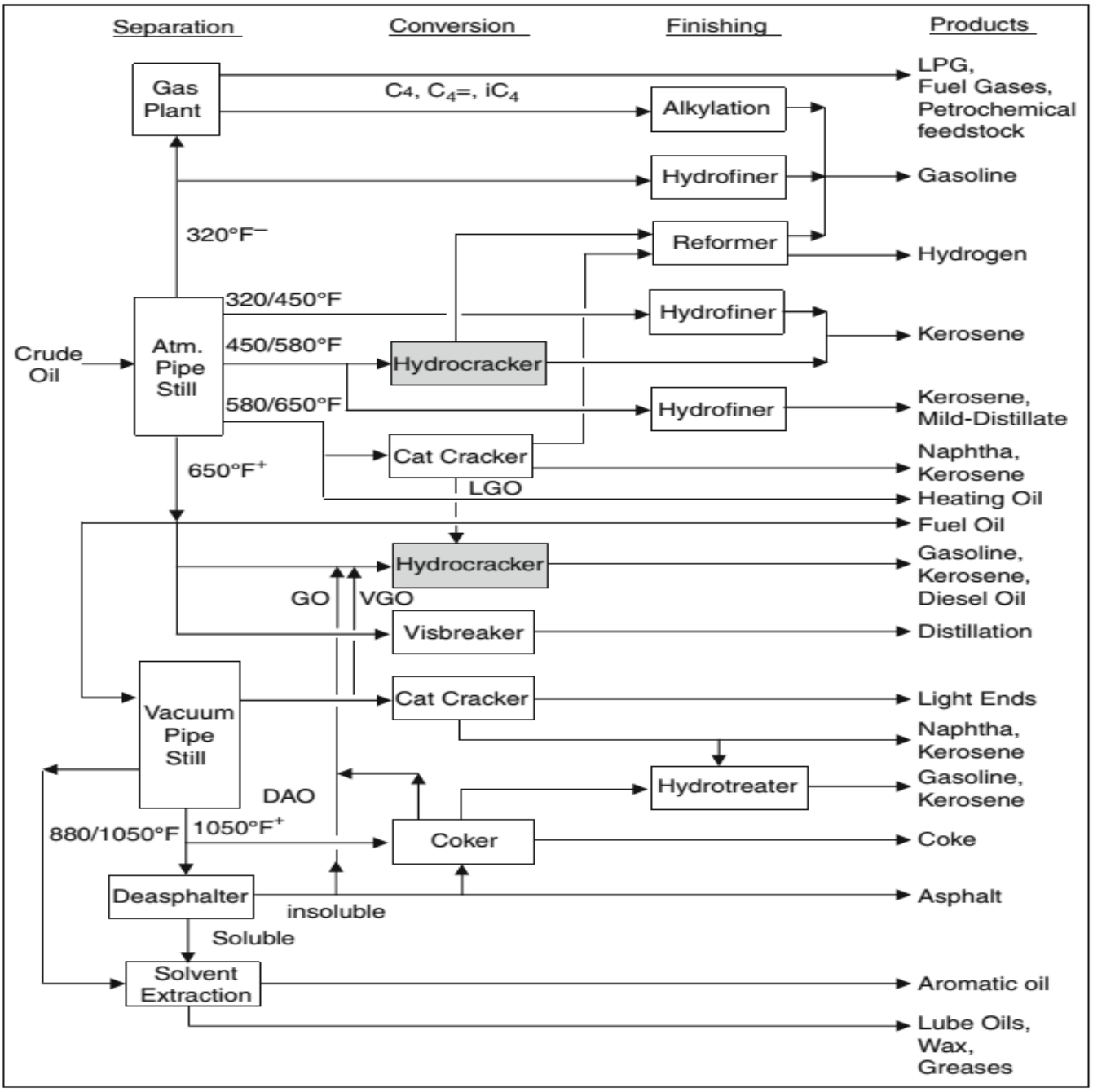


Figure 2.1: The purpose of hydrocracking in oil refinery [8]

2.1.2 Types of feed used in hydrocracking processes

Mainly for the hydrocracking process, the feed used is Vacuum Gas Oil (VGO). In addition to VGO, other types of feed are used of course, the type of feed used affects the product type and quality, different type of feed used is shown in Table 2.1 below.

Table 2.1:Feed Stocks and Products of hydrocracking processes[9]

Feedstocks	Products
Kerosene	Naphtha
Straight-run diesel	Naphtha and/or jet fuel
Atmospheric gas oil	Naphtha, jet fuel, and/or diesel
Vacuum gas oil	Naphtha, jet fuel, diesel, lube oil
FCC LCO	Naphtha
FCC HCO	Naphtha and/or distillates
Coker LCO	Naphtha and/or distillates
Coker HCO	Naphtha and/or distillates
Deasphalted oil	Olefin plants feedstocks

2.2 Slurry phase bed reactor

There are two well-known technologies available for hydrocracking of heavy oil, (i) fixed bed technology and (ii) slurry processes. The conventional refineries use fixed bed processes where the feeds and hydrogen are passed through a fixed catalyst bed to produce lighter products. In slurry process, both the catalyst and feed are well mixed inside the reactor. The slurry process can handle high impurities crude, which is common in heavy oils [3,4]. Another important advantage of slurry process is the intimate contact between the catalyst and the feed due to the movement of the smaller size catalysts inside the reactor. The available surface area of the slurry catalyst is also higher because of the well mixed feed and catalyst, which minimizes the mass transfer limitations. The slurry process also provided with the option of catalyst regeneration/refill, as it allows withdrawing from and re-entering the catalyst into the reactor. This way, the reaction can be controlled to achieve desired products[6].

2.3 Dispersed metal catalyst

Generally, the dispersed metal catalyst for hydrocracking process can be divided into two main categories (heterogeneous and homogenous). The heterogeneous catalyst is mainly solid powder, while the homogenous catalyst is in the liquid phase and classified into oil soluble and water soluble. Precursors used for oil soluble catalyst are mainly transition metal compounds. The main compounds used are metals naphthenates such as Molybdenum naphthenate, Cobalt naphthenate, and Nickel naphthenate. Other compounds are used such as Molybdenum and Nickel acetyl acetones. While for water soluble catalyst metals nitride is the main compound used. Such as Cobalt nitride, Nnickel nitride, and Ferric nitride . Other compounds are also used

as catalyst precursors such as Phosphomolybdic and Ammonium tugestenate. Table (2.2) below show the most common catalyst precursors compound used in the literature[6].

Table 2.2: Most common transitions metal compounds precursors for dispersed catalysts [6]

Oil soluble	Water soluble
Molybdenum dithiocarboxylate	Cobalt nitride
Iron naphthenate	Nickel nitride
Cobalt naphthenate	Ferric nitride
Nickel naphthenate	Ammonium molybdate tetrahydrate (AMT)
Molybdenum naphthenate	Phosphomolybdic acid (PMA)
Iron pentacarbonyl	Ammonium tungstate (AT)
Mo and Ni acetylacetonates	Ammonium heptamolybdate (AHM)
Molybdenum 2-ethyl hexanoate	Ammonium tetrathiomolybdate (ATTM)

2.4 Thermodynamics and reactions kinetics

2.4.1 Thermodynamics

Most of the chemical reactions that are taking place in hydrocracking process are exothermic. Such as hydrocracking of paraffin or aromatic saturation by the addition of hydrogen. Because of this exothermic reactions temperature control inside the reactor should be considered in the design of hydrocracking reactor specially, fixed bed reactors. The issue of controlling the temperature inside the reactor is usually handled by using a quench of hydrogen gas between the beds of the reactors. Along with the availability of temperature indicators and temperature indicator controller to ensure a tight control of the reaction. In the case of high temperature, The catalyst will be lost. Table 2.3 below shows the heat of reaction for different hydrocracking reactions at 400° C [9].

Table 2.3:Heat of reaction for different hydrocracking reactions [9]**.**

Type of the reaction	Average heat of reaction at 400° C (kJ/mol)
Aromatics hydrogenation	210
Paraffin hydrocracking	46 to 58
Naphthenes hydrocracking	42 to 50
Aromatics hydroalkylation	42 to 46

2.4.2 Kinetics

Regarding the conversion for the hydrocracking reactions the following equation can be used in order to calculate the conversion [9]:

$$\%\, Conversion = \left(\frac{(EP+)feed-(EP+)products}{(EP+)feed}\right) \times 100$$

EP^{+} is the fraction of material in the feed or product boiling above the desired end point usually as wt% or vol%.

The nature of the reactions that might occur in the hydrocracking reactions is complicated because most of the reactions are consecutive reactions. So it will be a hard mission to study the kinetics for the hydrocracking reactions, because of that there is just a few literature on this topic [9]. Recently there is a number of mathematical models proposed in order to cover all the possible reactions that might occur in the hydrocracking reactions. Such as VR hydrocracking

reactions which are presented as net of reactions as in Figure (2.2) below. However, a study done by Filimonov et al in 1972 [14] for the hydrocracking of polyaromatics and naphthenes is shown in Figure (2.3).

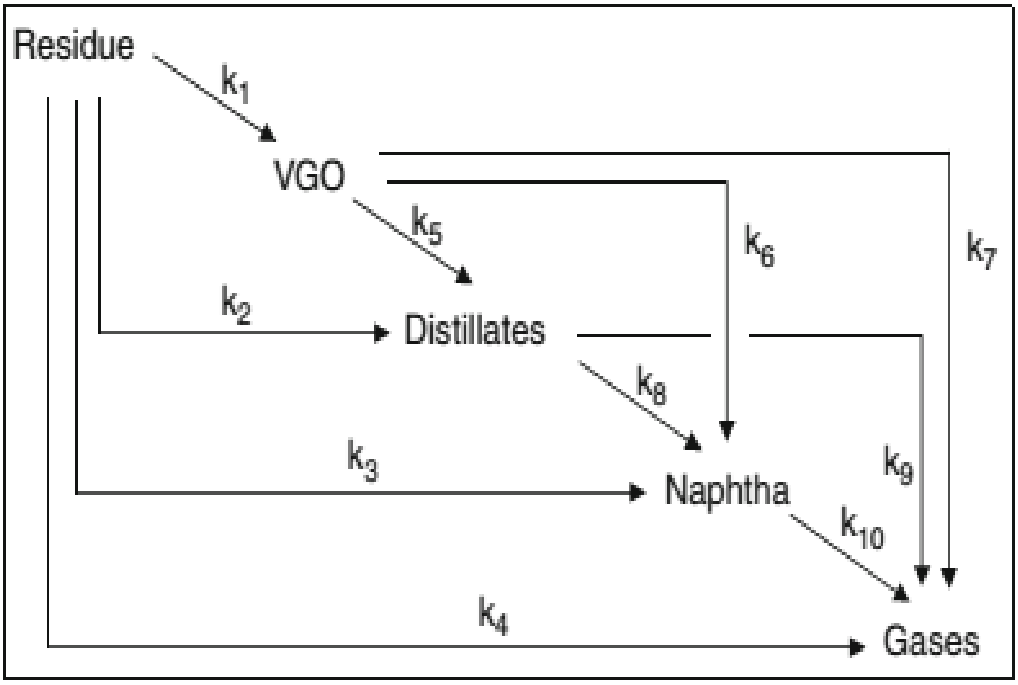


Figure 2.2: Proposal of a kinetic model for the hydrocracking of vacuum residue [8].

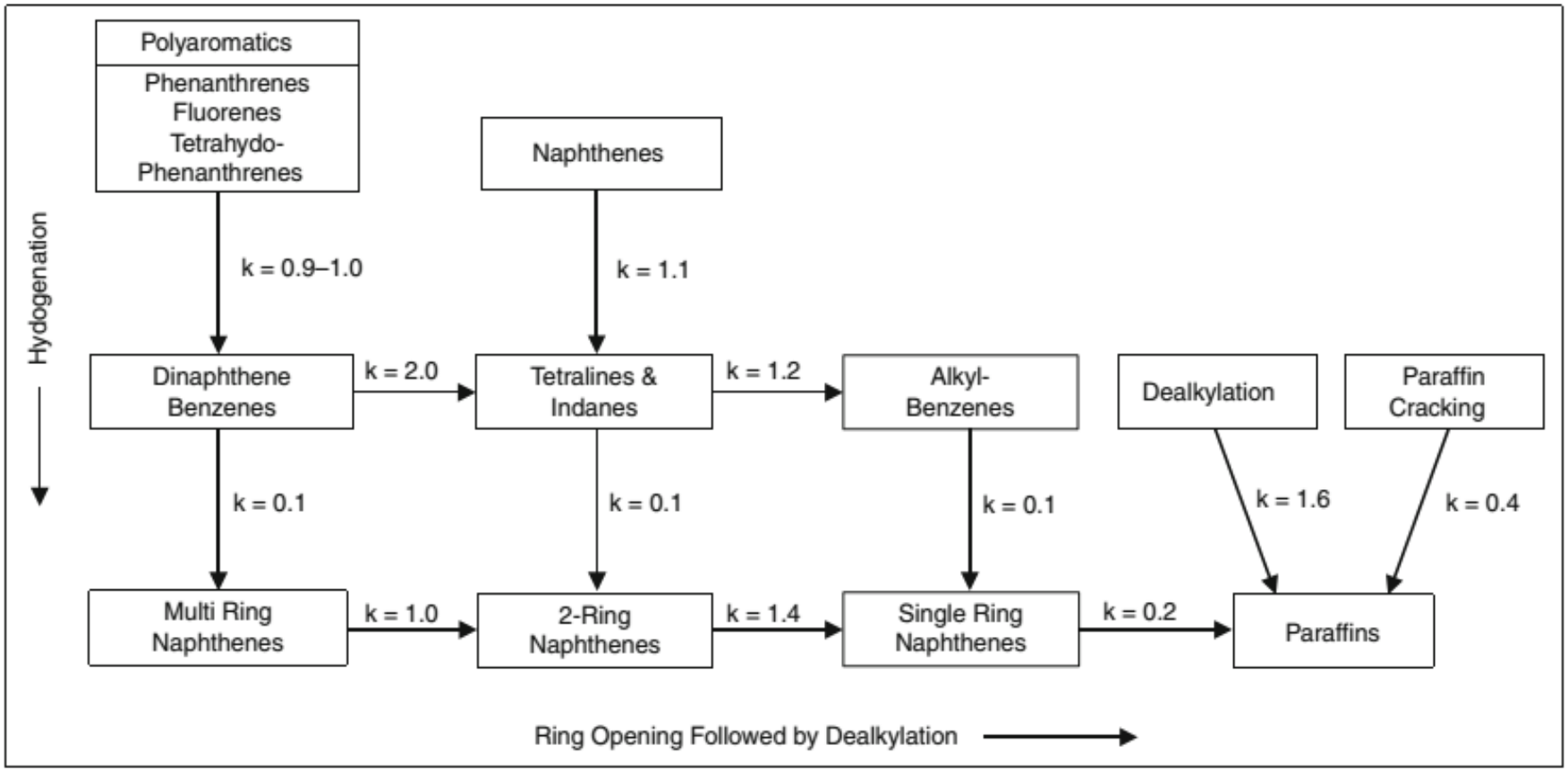


Figure 2.3: Relative rate of reaction under hydrocracking conditions [9].

2.5 Effects of different parameters in the reaction

The amount of catalyst precursor being used in the literature varies in the range of (twenty to one-thousand ppm) basis on the metal. But in general, the concentration has to be in the range of about 50-250 ppm. The major problem with increasing the concentration is that it will increase the formation of coke as it has been reported by Panariti in 2000 [15].

Panariti studied the effect of the concentration using molybdenum naphthenate as a precursor, he noticed that when using a different range of temperature the amount of coke formation increases with the increase of concentration . Panariti also noticed that neither the increase of catalyst concentration nor the increase of hydrogen pressure will affect the distillate production as can be shown in the Figure (2.4) below.

Another study conducted by Ortiz-Moreno [10] showed that the increase of catalyst to oil ratio by using ammonium tetra thiomolybdate as a catalyst precursor . They used Maya crude as a feed by fixing the pressure at 55 bar with a temperature range of 390 to 400 ◦C. They noticed that the catalyst to oil ratio of 330 ppm and the temperature can be used to control the variety of products such as (gasoline , LPG..etc).

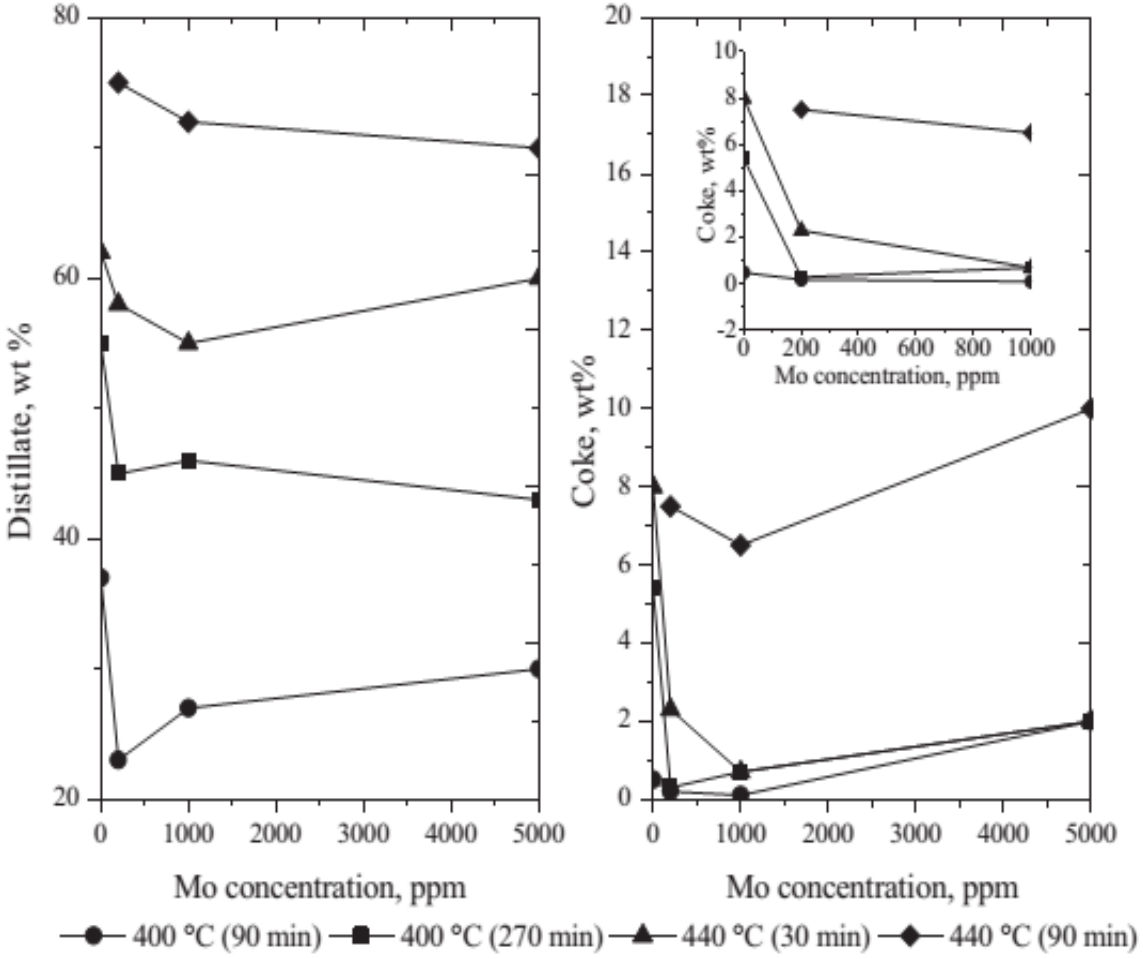


Figure 2.4: Consequence of increasing catalyst loading using Mo as a catalyst [5].

2.6 Supported versus dispersed catalyst

Generally, comparing the dispersed catalyst with the supported one, the advantages of dispersed catalyst can be summarized in the following points: Mainly the dispersed catalyst is less disposed to deactivation issues because it will not suffer from pore blocking problems. In addition to that, the dispersed catalysts will certainly have no diffusion problem as for supported catalyst and that will facilitate the reaction of larger molecules which are supposed to crack into smaller molecules. Beside to that the dispersed catalyst could reduce the coke formed by blocking free radicals [6].

2.7 Pyrolysis versus hydrogenolysis

The Major difference between pyrolysis and hydrogenolysis is that pyrolysis is (Thermal cracking, without catalyst and hydrogen) and hydrogenolysis is (Catalytic hydrocracking and that, of course, means using pressurized hydrogen and either supported or dispersed catalyst). In one hand in the thermal cracking process always a specific amount of high molecular weight petroleum product is formed such as coke and cracked residuum beside the desired light fuel such as jet and kerosene. In the other hand in the hydogenolysis process polymerized products can be avoided totally or decreased to a specific amount. Of course when the amount of coke decreased the amount of distillate will be increased. The type of compounds that result from the process of the coke formation such as naphthalene and other products are usually cracked in the presence of the catalyst. Then hydrogenated with the hydrogen which exists in the process, then these high molecular weight compounds become lower molecular useful products[16].

The process of hydrocracking increases the amount of the lighter product and decreases the formation of coke. Comparing with hydrotreating for example hydrocracking process severity is higher but it is an indispensable process because of the high valuable products produced, and the conversion of the oil comparing to other processes. Figures (2.5) and (2.6) below show the severity and the conversion of hydrocracking process comparing to other processes.

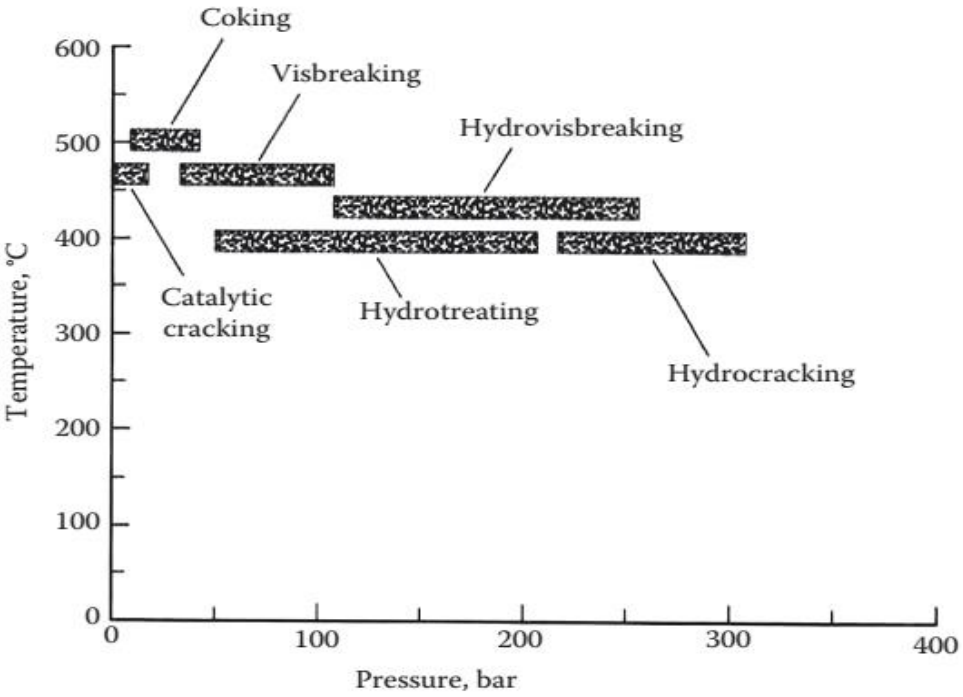


Figure 2.5: Conditions for hydrocracking comparing to other processes [12].

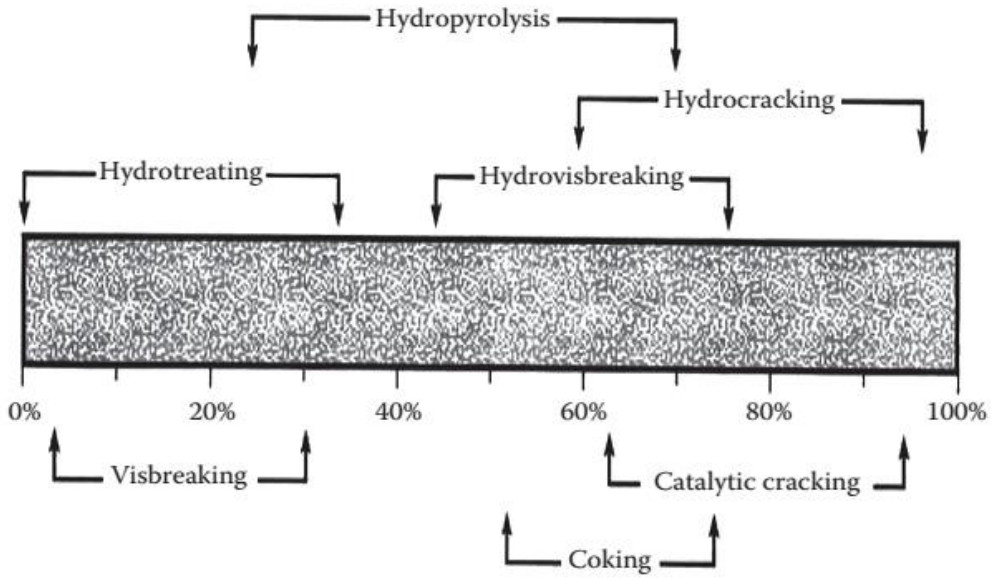


Figure 2.6: Conversion of hydrocracking process comparing to other processes [12].

2.8 Dispersed catalysts in hydrocracking

Table (2.4) shows a summary of different works done in heavy oil upgrading using dispersed metal catalysts. The common studied catalysts are transition metals, a chemical used as a catalyst precursor, the feed, and the reaction conditions, which includes reaction temperature, pressure and reaction residence times. It also contain the concentration of the catalyst in the feed and in some cases the speed at which the motor is running in round per minute (rpm).

By reviewing the work that has been done in heavy oil upgrading using dispersed metal catalyst, one can notice that the most used transition metal is Molybdenum. Molybdenum can either be used alone or with another transition metal in order to investigate the synergetic effect off adding two transition metals together. The most used transition metals to study synergetic effect with

Molybdenum are Nickel and Cobalt. Other transition metals used in addition to Molybdenum are mainly Nickel(Ni), Vanadium(Va), Potassium(K), Cobalt(Co), Tungsten(W), and Ferrous(Fe).

Oil soluble catalyst is more efficient catalyst in terms of activity but water soluble is more investigated because it is cheaper and more available than the oil soluble. Different kinds of feed used to investigate heavy oil upgrading using dispersed catalyst such as Maya Crude (Canada), Arab light Vacuum residue, Athabasca oil, sands bitumen, Karmany vacuum gas oil, Karmany atmospheric residue and Hamaca crude oil.

The conditions optimized in one type of crude, of course, will not be the best for another crude. But generally, there is no huge difference, especially in the temperature and pressure. The lowest temperature used was 300°C and the highest temperature used was 420°C. Regarding the pressure the range of pressure used is from 4 to 8 Mpa and in one case 11 Mpa was used with ferrous as transition metal [17].

For the concentration of the catalyst in the feed wide range of concentration was used ranging from 300 ppm up to 1800 ppm in one case but the most used concentration is ranging from 300ppm to 600 ppm. The speed of the motor is not mentioned in the majority of the works and it seems to be an unimportant factor. The last condition is the residence time used for the batch reactor it varies in a wide range but the most used residence time is 1 hour.

Table 2.4: Summary of different work done in heavy oil upgrading using dispersed metal catalyst.

Catalyst	Metals	Chemical used	Feed	Reaction Condition	References
V_2O_5,NiO	Ni, Va	AMV Ammonium meta Vandate (NH_4VO_3) ,Nickel nitrate hexahydrate $Ni(NO_3)_2$.6H2O	20%wt Arabian Vacume Resdue and 80%wt Arabian Vacume gas oil	(T 300° C) (vented to atmosphere) (160 rpm for 24 hr)	[18]
MoS_2	Mo	Ammonium tetrathiomolybdate, ammonium hepta molybdate	Maya Crude (Canada)	(T 400° C for 4 h) (P 800 Psi) (330 ppm Mo)	[10]
-	K, Ni	Potasium hydroxide, nickel(II) acetate tetrahydrate	Arab light Vacume Residue	(T 430-445 °C) (P 260 psig) (LHSV 5-10.5 h-1) (600 ppm catalyst) (K/Ni ,3:1 wt)	[19]
-	Ni,MO	nickel chloride , ammonium molybdate	Low sulfur waxy residue oil	(T 340 °C) (P 7 Mpa)	[20]
MoS_2	Mo	ammonium heptamolybdate, molybdenum chloride	Cold Lake Vacuum Residue	(T 415-445 °C) (P 13 Mpa) (100, 300, 600, 900 and 1800 ppm of Mo)	[21]
Layered ammonium cobalt molybdate $[(NH_4)HCo2(MoO_4)2 . (OH)_2]$	Co,Mo	ammonium heptamolybdate $[(NH_4).6Mo_7O_{24} .4H_2O)]$,cobalt nitrate$(Co(NO_3)_2).6H2O]$	Athabasca Oil Sands Bitumen	(T 420 °C) (7Mpa)	[11]
MoS_2	Mo	molybdenum naphthenate	Karamay vacuum gas oil	(T 420 °C) (8Mpa)	[13]
WS_2	W	$W(CO)_6$,, trimethylamine N-oxide,oleylamine, hexadecylamine ,carbon disulfide	-	(T 330 °C)	[22]
NiS	Ni	Nickel chloride $[NiCl_2 \cdot 12H2O]$	Karamay atmospheric residue	(T 435 °C) (P 7 Mpa)	[23]
$Fe_3(CO)_{12}$	Fe	$Fe_3(CO)_{12}$	Hamaca crude oil	250 ppm of Fe Temp (410–420 °C) P (11 MPa) residence time of 1 h.	[17]

2.8.1 Activity of different catalysts

Study done by Xu, Y., et al in 2009 using Karmany crude oil in order to know the order of activity of different water soluble catalyst, using preesure of 6Mpa and Temerature of 420◦C for 1 hour as reaction time, follow is a summary of this work: “Various commercial compounds containing a transition metal were evaluated: cobalt naphthenate (CoNaph), iron naphthenate (FeNaph), nickel naphthenate (NiNaph), phosphomolybdic acid (PMA), ammonium molybdate tetrahydrate (AMT), cobalt nitride ($Co(NO_3)_2$. 6 H2O), ferric nitride ($Fe(NO_3)_3$. 9H2O), ferrous sulfate ($FeSO_4$ .9 H_2O), nickel nitride (Ni(NO3)2 6 H2O), and ammonium tungstate (AT). All these catalyst precursors are analytical grade”[24].

‘’The comparison of different water soluble catalysts gives the following order of activity: $Co(NO_3)_2$ > AMT > $Ni(NO_3)_2$ > $FeSO_4$ > PMA > AT > $Fe(NO_3)_3$,,.[24]“In general, the overall performance of water-soluble multimetal composite catalysts is better than the corresponding single one or the oil-soluble one. The activities of several high performance catalysts obey this order: Mo/Co > Mo/Ni > CoNaph > NiNaph > Co(NO3)2 > Ni(NO3)2 > AMT”[24].

Promotion effect or synergetic effect for the dispersed metal catalyst as mentioned earlier is very important factor in the hydrocracking reactions. Different studies conducted lately in order to investigate the best combinations of metals in terms of activity. A Recent study was done by Christophe Geantet in a batch reactor[25], using atmospheric residue as a feed and 450°C as reaction temperature, while using a range of concentration from 300 ppm to 900 ppm and residence time of 1h. In order to study the promotion effect for the dispersed metal catalyst, three metal salt precursors were used which were V, Mo, Ni. Before studying the promotion effect of the metals the effect of just one metal was measured to be the basis of the comparison later on.

On the one hand, when mixing Mo metal precursor with Ni metal precursor an enhancement was noticed in the conversion of the atmospheric residue and its degree of hydrodesulphurization. On the other hand the effect of mixing Mo metal precursor with V metal precursor there was no synergy effect noticed and the effect was just the sum of the effect of the two metal precursors. The reason why mixing of Mo with Ni metal catalyst gave the synergetic effect is because of MoS_2 were found depositing on Ni_3S_2 surface and that was noticed by using high resolution transition electron microscopy (HRTEM) beside using X-ray adsorption spectroscopy (XAS).

2.9 Conclusion

From the reviewed literature, it is clear that hydrocracking is an indispensible process in oil refineries in order to upgrade the heavy oil to compensate the increasing demand for the fuel. The conventional fixed bed hydrocracking technology is used widely in the world, which has some limitations. Especially, the problems associated with the coke formation is signification which causes the catalyst deactivation and reactor fouling.

Different technologies were developed recently in order to overcome the catalyst troubles such as slurry phase hydrocracking and ebullated-bed technology, which are using dispersed metal catalyst. The dispersed metal catalysts are not fully understood and need more investigations. The dispersed metal catalyst was used in the beginning of twenty century in the liquefaction of coal. However, coal liquefaction processes were not developed since they were not economically feasible. With the end of liquefaction processes the research and development in the dispersed metal catalyst also ended. Recently different researches were conducted in order to fully

understand and develop the optimum dispersed metal catalyst for the heavy oil upgrading specially hydrocracking process.

Most of the researches conducted were focusing in the precursor which will lead to the least coke formation and highest conversion, the effect of eaction parameters such as temperature , pressure, a catalyst to feed ratio and reaction time was studied in different works using different feed. There is a consensus that Mo metal precursor has the highest activity among other metal precursors, and using other metal precursors such as Ni or Co metals precursors will enhance the properties of Molybdenum sulfide which is considered as the main catalyst for the hydrocracking process. Not all metals were fully investigated for the hydrocracking reactions, one of these metals is Tungsten and Cobalt, and this could be because of the rarity of their metal precursors.

Oil soluble precursors are less investigated than water soluble precursors because water soluble precursors is cheaper and more available than oil soluble precursor although that oil soluble precursors have higher activity, conversion and the coke formed is lower.

CHAPTER 3

EXPERIMENTALS

The objective of this work is to investigate Cobalt (Co), molybdenum (Mo) and Iron (Fe) metals as dispersed catalyst for heavy oil upgrading at modest reaction conditions using batch reactor. In order to well investigate the effect of those metals and to make it as a base line, the effect of thermal hydrocracking without using any catalyst was investigated firstly, after that thermal hydrocracking compared with catalytic hydrocracking in order to investigate the most appropriate catalyst could be used for the reaction. Different factors were taken into consideration when it comes to catalyst evaluation such as coke formation, conversion, product distribution and other different factors. Table 3.2 below summarizes the type of the reactor, conditions that used in experiments, catalyst concentration range, and residence time for the reactions. Table 3.1 summarizes the catalyst precursors used.

Table 3.1: Summary of the Metal used with the catalyst precursor.

Metal	Catalyst Precursor
Co	cobalt 2-ethylhexanoate
Mo	molybdenum 2 ethylhexanoate
Fe	Iron naphthenate

Table 3.2:Summary of the reactor type and the conditions.

Type	Batch Stirred Reactor
Temperature	390^{o}C -450^{o}C
Pressure	Starting pressure of 4 MPa
Feed	VGO
Feed quantity	30 gm
Catalyst Concentration	300-1000 ppm (wt)
Time for the run	30 min -90 min

3.1 Thermal runs

As mentioned earlier, a set of non-catalytic reactions were conducted for the feed which is VGO, as a base line or reference to compare with catalytic reactions, and study the effect of the dispersed metal catalyst that used. Besides being a reference the sets of experiments in this part is designed to study the effect of temperature on thermal hydrocracking reactions, and compare it later with the effect of temperature on catalytic reactions. Feed of 30 gm heavy VGO used with 420 ^{o}C as reaction temperature and 4 MPa was used as starting pressure for the hydrocracking experiments.

3.2 Catalytic runs

This part is divided into two sections: the first section is designed in order to investigate the effect of mono dispersed metal catalyst of Co, Mo and Fe using oil soluble precursors. In the second section promotion effect was studied using the same metal precursors used in the first section along with solid catalyst.

3.2.1 Hydrocracking of VGO using dispersed catalysts

In this section as mentioned earlier the study was done on different mono dispersed metal catalyst in order to study the effect of each metal used in the conversion and the amount of coke formed, in addition to the effect of the metal used this section is also designed to study the effect of precursor concentration in the feed, noticing that the temperature and the starting pressure was fixed in this part in order to study the effect of the metal used and the concentration alone. Table 3.3 below shows the set of designed experiments for this part.

Table 3.3: Set of designed experiments for catalytic mono dispersed catalyst.

Run No	Temperature(^{o}C)	Starting Pressure (bar)	Feed Quantity (gm)	Metal used	Metal Concentration ppm (wt)
2.1.1	420	50	30	Co	300
2.1.2	420	50	30	Co	500
2.1.3	420	50	30	Co	1000
2.1.4	420	50	30	Mo	300
2.1.5	420	50	30	Mo	500
2.1.6	420	50	30	Mo	1000
2.1.7	420	50	30	Fe	300
2.1.8	420	50	30	Fe	500
2.1.9	420	50	30	Fe	1000

3.2.2 Hydrocracking of VGO using dispersed catalysts with a solid catalyst

As mentioned earlier this part is designed to study the effect of adding dispersed metals catalyst to solid catalyst, in order to study the promotional effects of the different metals , so the concentration of dispersed metals and different amounts of solid catalyst was used with fixed concentrations. Table 3.4 summarizes the set of experiments conducted in this part, noticing that the conditions used in this part was fixed as the same conditions in the previous section which

are 420°C for the temperature and 4MPa as starting pressure, and residence time was fixed in one hour for all the experiments.

Table 3.4: Set of experiments used for solid with the dispersed metal catalyst.

Run No	Supported cat Cat /Oil ratio	Metals used	Metal Concentration ppm (wt)
2.2.1	0.1	-	-
2.2.2	0.1	Mo	Mo (500)
2.2.3	0.1	Co	Co(500)
2.2.4	0.025	-	-
2.2.5	0.025	Mo	Mo(500)
2.2.6	0.025	Co	Co(300)

3.3 Kinetics experiments

After selecting the best metal used in hydrocracking of VGO, then sets of experiments was done in order to study the kinetic of the dispersed metal catalyst, by using the catalyst which gave the best performance regarding the conversion and the coke formed. Table 3.5 below summarizes the sets of experiments conducted in this section

Table 3.5: Summary of experiments conducted for the kinetic study.

Run No	Time for the reaction (min)	Temperature (^{o}C)
3.1	30	390
3.2	60	420
3.3	90	450
3.4	30	390
3.5	60	420
3.6	90	450
3.7	30	390
3.8	60	420
3.9	90	450

3.4 Experimental procedure

The heavy oil hydrocracking experiments have been conducted in a batch autoclave reactor. A schematic diagram of the reactor and its components are shown in Figure (3.1) while, Figure (3.2) presents the details experimental steps.

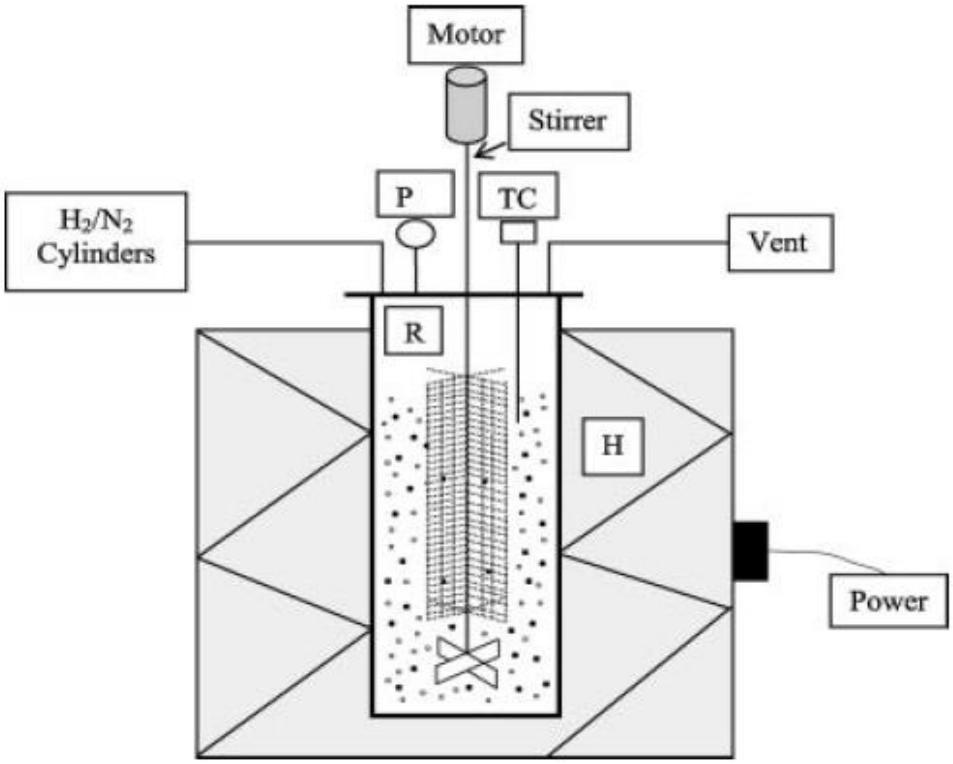


Figure 3.1: Experimental setup of the batch process.

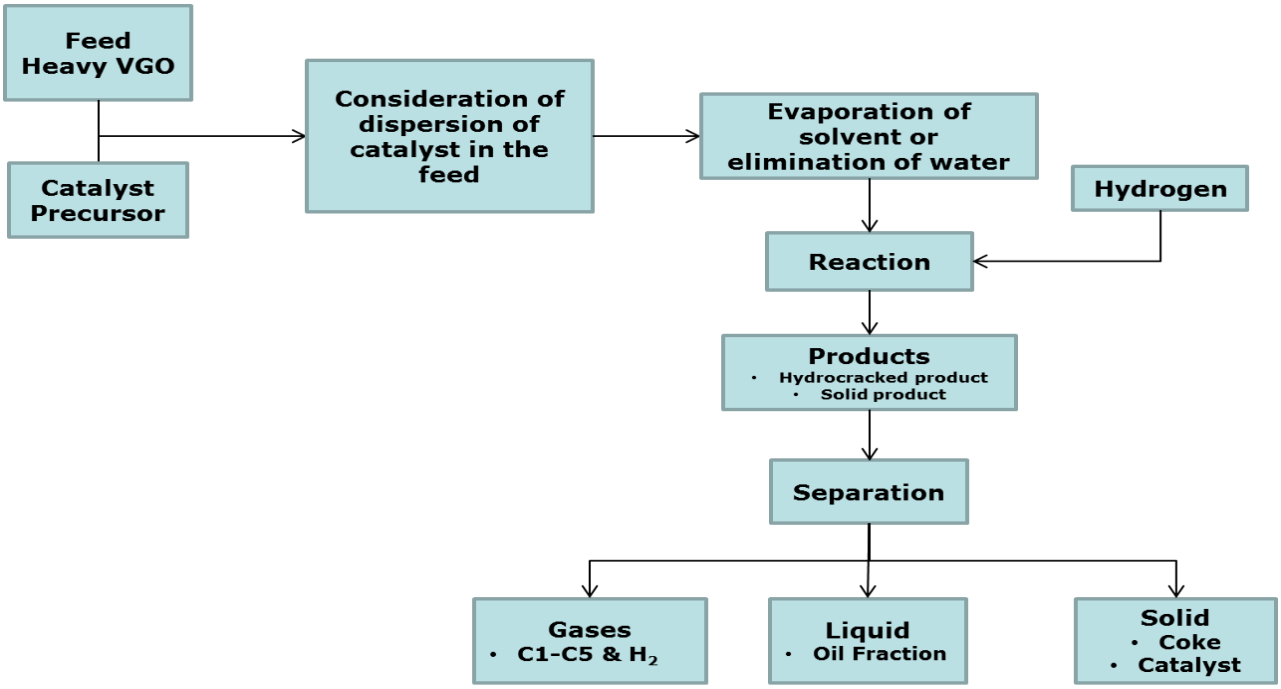


Figure 3.2: Experimental steps involved in hydrocracking of VGO using oil soluble dispersed catalysts.

For each experiment, the desired amount of feed VGO was mixed with a specific amount of catalysts precursor (dispersed and/or supported) and the mixture was transferred to the reactor. Following the leak test with nitrogen, the reactor was purged three times using hydrogen to make sure that there is no air inside the reactor. The reactor was then heated to the reaction temperature (~ 420 °C) at low hydrogen pressure to minimize the reaction during the heating period.

After that the stirrer was started (950 rpm) to ensure proper mixing of catalyst, feed and hydrogen inside the reactor. The reaction was then allowed to continue for one hour. Following one hour reaction, the system was allowed to cool down to room temperature and samples (products and spent catalysts) were collected. The gas sample containing H2 and C1-C5 hydrocarbons was analyzed using a GC equipped with both FID and TCD detectors.

3.5 Gas and liquid product analysis

The gas sample containing H_2 and C_1-C_5 hydrocarbons was analyzed using a GC equipped with both FID and TCD detectors. The liquid product was analyzed by using a thermogravimetric analyzer (TGA) to determine product distribution as follows: naphtha: 90-221°C; distillate: 221-343 °C; VGO: 343-565° C [26]. The conversion of VGO was defined as the sum of yields for light hydrocarbons (gas), naphtha and coke (Eq. 1). The unconverted material is defined as all liquid products with boiling point above 221 °C. The VGO conversion was calculated using the following equation (Eq. 1):

$$Conversion\ (\%) = \frac{W_{VGOf} - W_{VGOp}}{FW_{VGOf}} \times 100 \qquad (1)$$

where, W_{VGOf} and W_{VGOp} are the weight of VGO in the feed and product, respectively.

3.6 Spent catalyst analysis

The spent catalysts were analyzed using FTIR to confirm the in-situ sulfiding of the metal precursor are reaction conditions. The FTIR spectroscopy analysis were recorded using Nicolet 6700 Thermo Fischer Scientific instrument. For each experiment, 3 mg of samples were mixed thoroughly with 400 mg KBr. Thereafter, infrared spectra of the samples were collected in the range 400 cm^{-1} to 4000 cm^{-1}. The morphologies of the spent and the fresh catalysts were studied by using a scanning electron microscope, (JEOL JSM-6460LV) operated at 5 kV equipped with energy dispersive X-ray (EDX). SEM was conducted for two samples of the spent catalyst with and without using dispersed metal catalyst in order to see the effect of the dispersed catalyst on the surface of the spent catalyst.

CHAPTER 4

RESULTS AND DISCUSSION

In this investigation the slurry phase hydrocracking of VGO was conducted using the oil soluble dispersed catalyst as (i) a standalone catalyst and (ii) an additive with a solid hydrocracking catalyst. The promotional effects of the oil soluble metal precursors were analyzed based on the product distribution and coke formation during VGO hydrocracking.

4.1 Standalone dispersed catalysts

Cobalt 2-ethylhexanoate, molybdenum 2-ethylhexanoate and iron naphthenate have been employed as oil soluble dispersed catalysts. All experiments were conducted with three different concentrations, i.e., 300 ppm, 500 ppm and 1000 ppm of these catalysts. FTIR was conducted in order to confirm that the metal precursor used was successfully sulfurized in-situ and the active metal sulfide was formed. Figure 4.1 shows the FTIR spectrum of the solid materials, which contains the coke and the formed catalyst of the specific catalyst precursor. The peaks appeared between 400 and 450 cm^{-1} indicate that metal precursors added were successfully transferred to metal sulfide (active phase).

The hydrocracking of VGO products are classified as gas (C_1-C_5), naphtha, distillate, coke and unconverted VGO and are shown in Figure 4.2. Figure 4.2 also includes the product analysis of the thermal hydrocracking run for comparison. Thermal runs resulted in 35% conversion of VGO. With the addition of dispersed catalyst the conversion value decreased close to 31%. This

VGO conversion was expected given the fact that the dispersed catalysts only contribute to the hydrogenation reactions. The cracking of the heavy hydrocarbon molecules still relies on the thermal energy. Therefore, the dispersed catalyst only increased the distillate fraction and decreased the gases product fraction. Among the three catalysts, Co and Mo based catalyst showed higher percentage of distillate and lower gaseous products. This result was expected given the hydrogenation activity of the dispersed metal catalyst helps to hydrogenate the cracked molecules contributing to the lighter products [27,28].

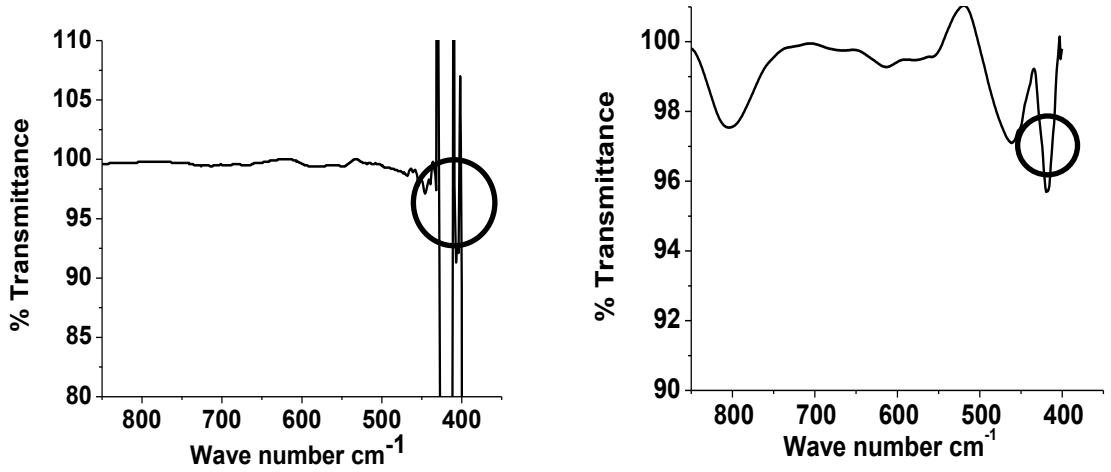


Figure 4.1: (a) Co catalyst FTIR spectrum, (b) Mo Catalyst FTIR spectrum.

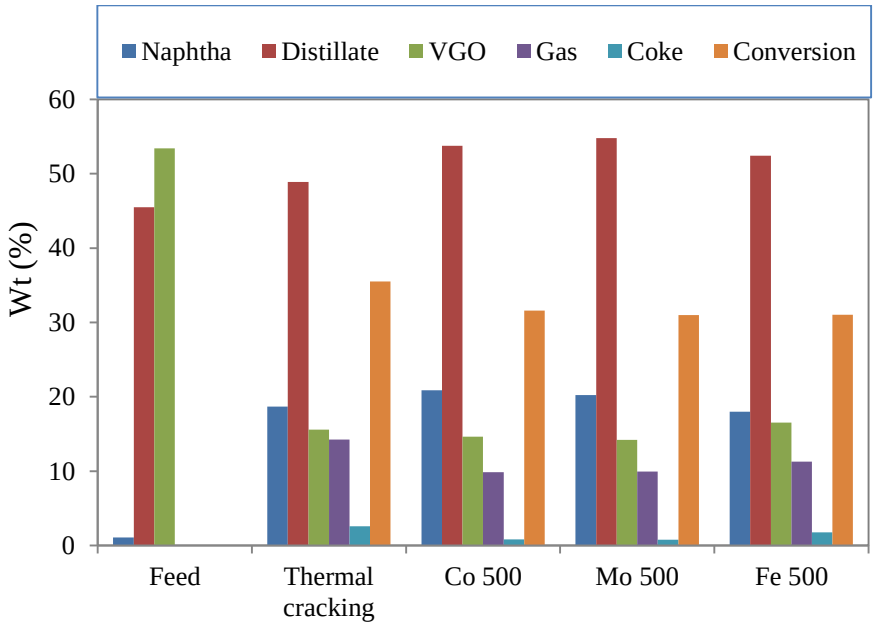


Figure 4.2: Product distributions (Feed: VGO, Catalysts: 500 ppm standalone dispersed catalysts, T: 420 °C; P: 8 MPa; Reaction time: 1 hr).

The amount of coke formed when dispersed metal catalyst used was expected to decrease comparing to thermal run because cracked intermediate free radicals hydrogenation will be enhanced with the dispersed metal catalyst [5,10]. Figure 4.3 reports the percentage of coke formation using cobalt, molybdenum and iron metal precursors at three different concentrations. It is clear that the amount of the catalyst significantly affect the coke formation. The type of metal precursor also has influence on the coke formation. In case of Mo and Co metal sulfides the lowest coke formation was achieved at 500 ppm catalyst concentration. On the other hand the Fe based showed lowest amount of coke formation at 300 ppm. However, the total coke formation with Mo and Co are much lower than the Fe catalysts. Previously, Joseph Wood et.al[29] also showed a lower activity comparing of Fe dispersed catalyst as compare to Mo based dispersed catalyst in decreasing the amount of coke formed and increasing middle distillate. For all three catalysts, high concentration shows inversed effects on the coke

formation. This could be explained by considering the crystal size and dispersion of the catalyst particles. The metal crystal dispersed in the vacuum gas oil could be responsible for seeding the precipitation of solids. The increased dispersed metal concentration can increase hydrogenation reactions, which can decrease the stability of asphaltene [30]. As a result, the formation of coke increased [15]. Therefore, optimum concentration of dispersed catalyst is crucial to minimize the coke formation [15].

Figure 4.4 shows effects of dispersed metal concentrations on products distribution. For comparison thermal experiments were also conducted as mentioned earlier. The yield of produced naphtha decreased with increasing dispersed catalyst concentrations. At 300 ppm catalyst concentration, both the naphtha and distillate fraction yields were increased as compared to the thermal run. The distillate yield decreased when concentration increased from 300 ppm to 500 ppm. While, increasing of dispersed metal catalyst above 500 ppm has no significant effect on the yield of the distillate. Amount of un-converted VGO increased significantly when the concentration of dispersed catalyst increased. Regarding the gas yield, 300 ppm catalyst concentration gave lower gas yields as compared to the thermal run. While, increasing of dispersed metal concentration increases the yield of the gas. This observation suggests that the excessive amount of dispersed catalysts is not helpful for increasing the lighter fractions.

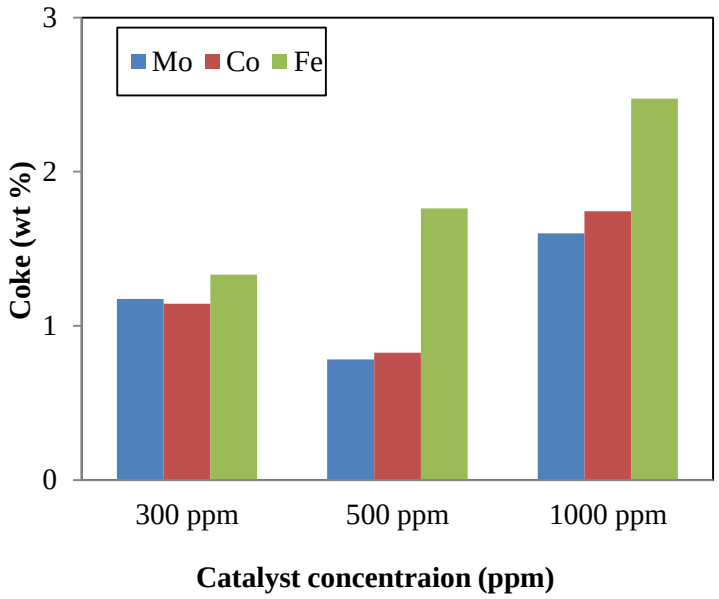


Figure 4.3: Coke formation using different concentration of cobalt, molybdenum and iron precursors (Feed: VGO, T: 420 °C; P: 8 MPa; Reaction time: 1 hr).

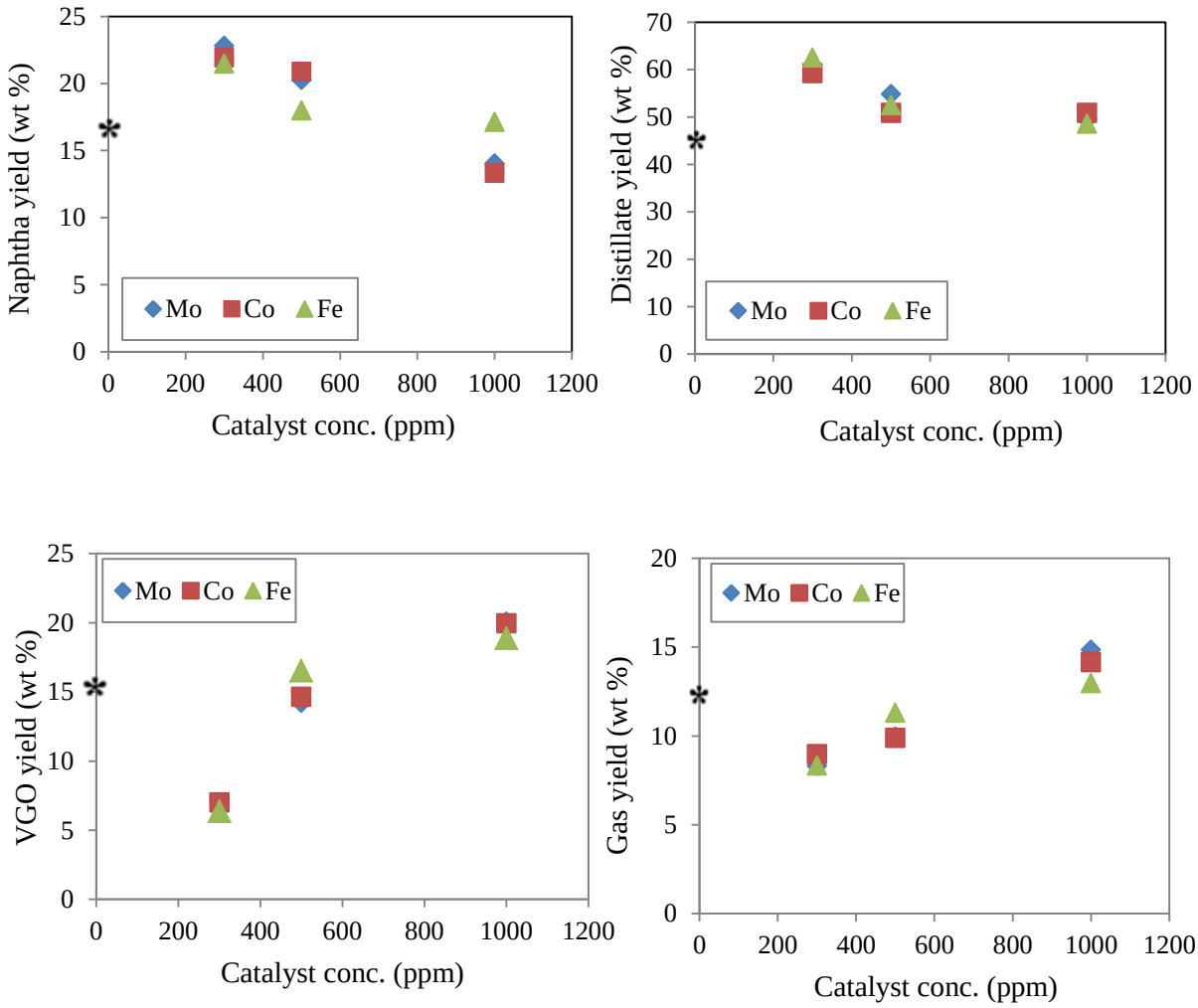


Figure 4.4: Product yields Product yields (wt %) (a) naphtha, (b) distillate, (c) VGO and (d) gas at different catalyst concentrations (Fe ▲), (Mo ◆) and (Co ■) (Thermal *) (Feed: VGO, T: 420 °C; P: 8 MPa; Reaction time: 1 hr)

4.2 Dispersed catalysts with supported catalyst

In co-catalyst experimental runs, a commercial first-stage hydrocracking catalyst (W-Ni/Al_2O_3-SiO_2) was used to demonstrate the promotional effects of the dispersed catalysts. The properties of the supported commercial W-Ni/Al_2O_3-SiO_2 catalyst are listed in Table 4.1. Two sets of

experiments are conducted: first, using only the supported catalysts while in the second set, both supported and dispersed catalysts were employed. Two different catalysts to oils ratios (1:10 and 1:40) were used in addition to the dispersed catalysts while the dispersed catalyst concentration was maintained at 500 ppm level.

Table 4.1: The properties of the supported catalyst that used for hydrocracking

Property	Unit	Value
Average Length	mm	1.90
BET surface area	m^2/g	288
Compacted bulk density	g/cc	0.71
Mean pore radius	Å	40.0
Pore volume	cc/g	0.56
Loss on ignition at 750°C	wt.%	9.6
Attrition loss	%	< 1
Side crushing strength	N/mm	35.0
Al_2O_3	(wt.%)	19.5
NiO	(wt.%)	1.13
SiO_2	(wt.%)	59.7
WO_3	(wt.%)	11.8

Figure 4.5 shows the effect of dispersed metal catalyst on product distribution when experiments were performed in the presence of supported catalyst. Unlike the standalone dispersed catalyst runs, the supported catalyst affects the product distribution due to the cracking reactions over the acidic sites. A 54% of VGO conversion was achieved at catalyst to oil ratio of 0.1. On the other hand 51% conversion was observed with C/O of 0.025. Therefore, only 0.025 C/O ratio is

enough to achieve the desired level of conversion. This increased conversion from thermal run was mainly due to the cracking reactions on the acidic sites of the supported catalysts followed by their subsequently hydrogenation on the dispersed catalysts. Thus, increased amounts of product in naphtha range were observed. On the other hand, in the case of 0.1 C/O coke formation are much higher than that of the 0.025 C/O runs, due to excessive cracking reactions.

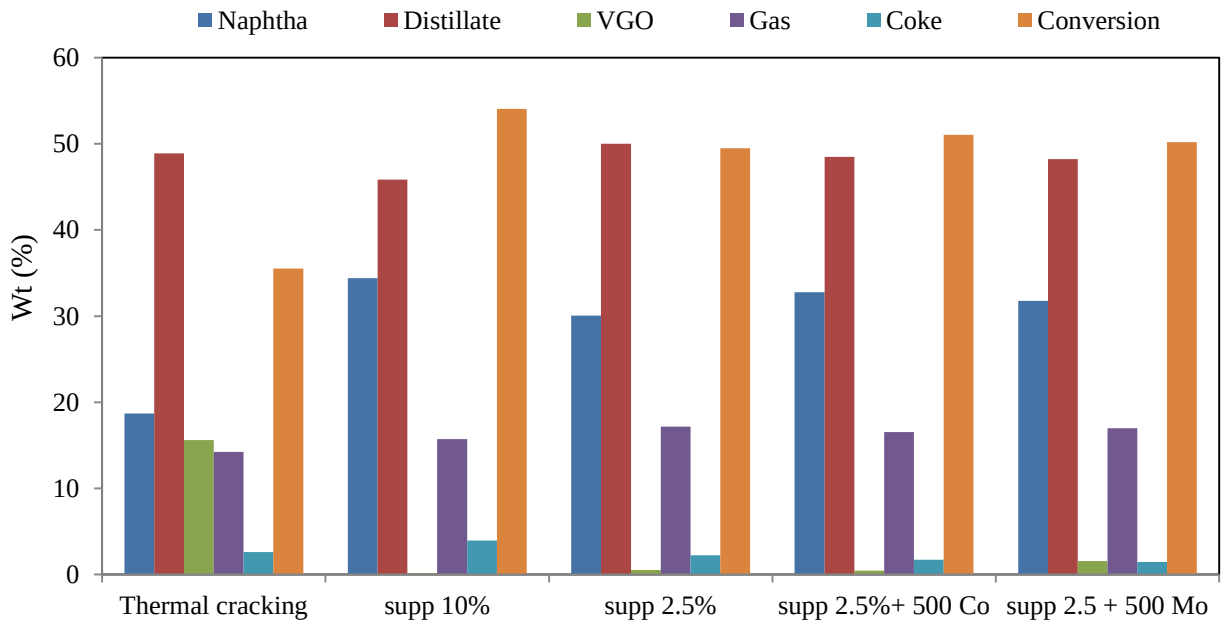


Figure 4.5: Effect of supported with dispersed metal catalyst on product distribution of hydrocracking reactions (Feed: VGO, T: 420 °C; P: 8 MPa; Reaction time: 1 hr).

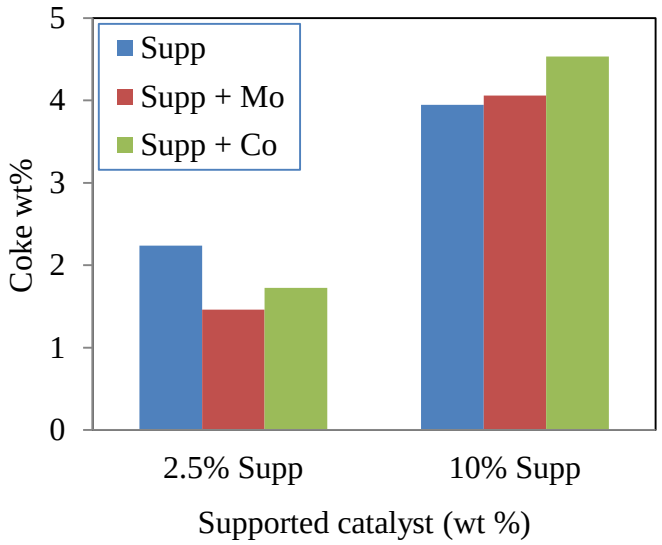


Figure 4.6: percentage of coke formed using different amounts of coke formed with different amount of supported catalyst combined with dispersed catalyst (Feed: VGO, T: 420 °C; P: 8 MPa; Reaction time: 1 hr).

At lower amount of supported catalyst, C/O of .025, addition of dispersed metal catalyst will decrease the amount of coke formed in hydrocracking process to less than 2 wt % when Co and Mo catalyst precursors were used As shown in Figure (4.6). This can be attributed to the dispersed metals sulfides which enhances the hydrogenation reactions. The reason why these dispersed metals sulfide didn't decrease the amount of coke formed in the case of 0.1 C/O ratio can be explained by that increasing metal sulfide concentration can increase hydrogenation reactions which can decrease the stability of asphaltene [30]. As a result the formation of coke formation increased [15].

The promotional effects of the dispersed catalyst can be explained using the conceptual mechanism presented in Figure 4.7. High molecular weight molecules undergo cracking either thermally or on the acid sites of the solid catalyst. These cracked molecules are not completely

hydrogenated by the solid catalyst and react together to form coke on the solid catalyst surface. This causes the blocking of the active sites and which leads to catalyst deactivation. The presence of dispersed active phases causes an increase in the hydrogenation of these coke precursor molecules and leads to lower coke production.

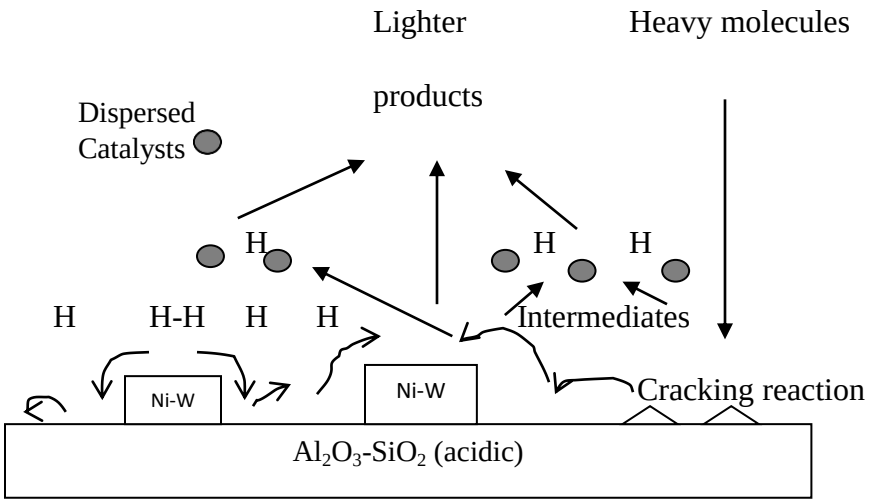


Figure 4.7: A possible mechanism of promotional effects of dispersed catalyst along with supported catalyst.

Figure (4.8) is a SEM image shows the active site of the supported solid catalyst before conducting any experiment; it appears that active sites of the solid catalyst are well distributed in the surface of the catalyst. Figure 4.9 (A) shows the spent solid catalyst at C/O of 0.025 without dispersed catalyst, while Figure 4.9 (B) shows the spent solid catalyst of the same C/O but with adding 500 ppm Co dispersed catalyst. Both experiments were conducted using the same conditions.

Comparing Figure 4.9 (A) and (B) it is appear that more amount of coke is deposited in the surface of the catalyst when dispersed catalyst was not used (A), which was expected since the dispersed catalyst will enhance the hydrogenation reactions which will lead to low amount of

coke formation. In figure 4.9 (B) we can also notice that the use solid catalyst has sintering problem and it also started to crack, so a catalyst with higher crushing strength is recommended to be used in the future works.

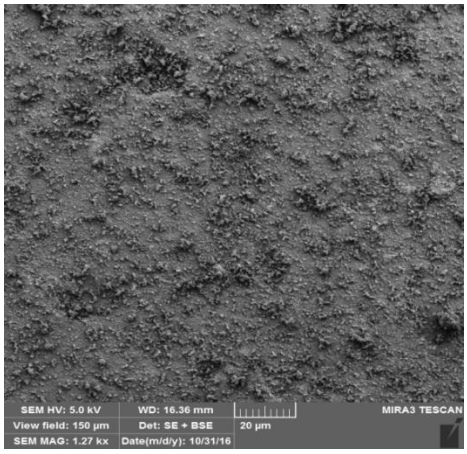
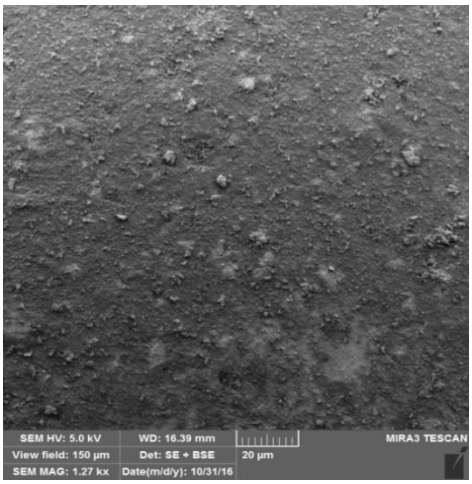
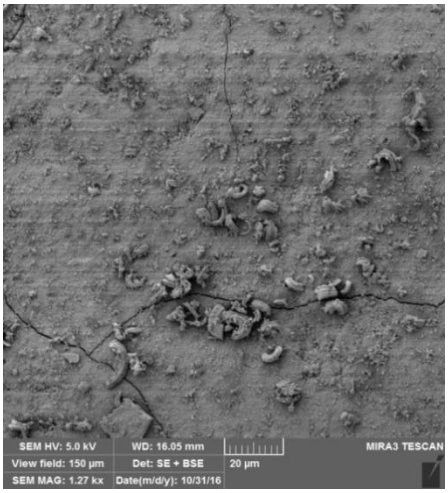


Figure 4.8: Supported solid catalyst





(A) (B)

Figure 4.9: (A) Spent catalyst of 0.025 C/O without dispersed catalyst , (B) spent catalyst of 0.025 C/O with dispersed catalyst (Co 500 ppm)

CHAPTER 5

KINETICS

This chapter presents the kinetic modeling of the slurry phase hydrocracking of VGO using batch reactor experimental data. A five lumped kinetics model was formulated based on the product distributions. The kinetics parameters are estimated by least-squares fittings of the model equation using experimental data implemented in MATLAB. The estimated parameters are evaluated based on their physical significances and various statistical indicators.

5.1 Reaction scheme

The nature of the reactions in hydrocracking processes are complicated. Most of the reactions are consecutive and there are many possibilities with different mechanisms involved [22,23]. Therefore, lumping of various product groups have been found to be effective for kinetic modeling of catalytic hydrocracking of VGO and other heavy residues [9]. In this investigation, a 5-lump model has been considered to represent the hydrocracking of VGO (Figure 5.1). This model considers that the cracking of VGO gives four major group of products including distillate, naphtha, gases and coke. The distillate is further cracked to naphtha and then to gases. Previous studies showed that the coke formation directly from VGO is much higher than the other routes [24, 25]. Therefore, the contribution of coke formation from the lighter products (distillate, naphtha and gases) is considered to be negligible.

Based on the above 5-lumped model, the rate of reaction for each reacting species can be written as:

Rate of disappearance of VGO:

$$\frac{dY_{VGO}}{dt} = -(k_1 + k_2 + k_3 + k_4)Y_{VGO}^2 \qquad (2)$$

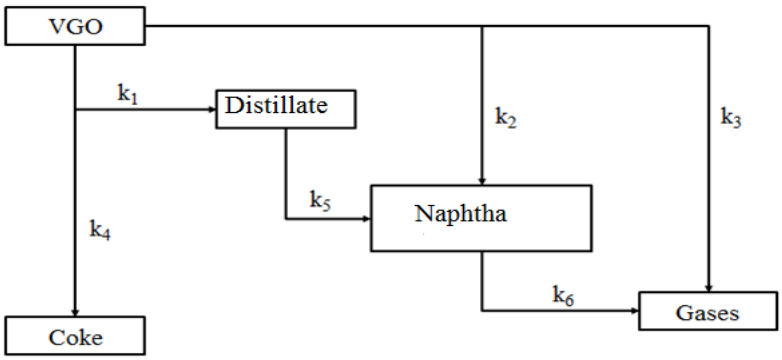


Figure 5.1: Proposed reaction scheme for hydrocracking of VGO

Rate of appearance of products (distillate, naphtha, coke and gas):

$$\frac{dY_{Distillate}}{dt} = \left(k_1 Y_{VGO}^2 - k_5 Y_{Distillate}\right) \qquad (3)$$

$$\frac{dY_{Naphtha}}{dt} = \left(k_2 Y_{VGO}^2 - k_5 Y_{Distillate} - k_6 Y_{Naphtha}\right) \qquad (4)$$

$$\frac{dY_{Coke}}{dt} = k_4 Y_{VGO}^2 \qquad (5)$$

$$\frac{dY_{Gas}}{dt} = \left(k_3 Y_{VGO}^2 + k_6 Y_{Naphtha}\right) \qquad (6)$$

where, Y_i are the product compositions,. It is important to note that hydrogen is used in excess, which makes it possible to replace the hydrogen weight percentage by 1 making the equations simpler. k_i are the temperature dependent rate constants given by Arrhenius equation (Eq. 7):

$$k_i = k_{i0}\exp\left(-\frac{E}{RT}\right) \qquad (7)$$

where, E is the activation energy (kcal/mol) and R is the gas constant.

5.2 Parameter estimation and kinetics evaluation

In parameter estimation, the developed models, the temperature dependent specific reaction rate constants were first combined with the kinetics model equations. The concentrations of various species were expressed in terms of mass fractions. The resulting differential equations were then numerically solved in conjunction with a least square fitting of the experimental VGO hydrocracking data obtained from the batch reactor. In solving the differential equation MATLAB ODE 45 subroutine (Runge-Kutta-Gill method) was employed, while the parameters were estimated using LSQCURVEFIT subroutine (Modified Marquad method).

Experiments were conducted at range of reaction temperatures (390 to 450 °C) and various residence times (30, 60 and 90 mins). In this fashion total two 45 data points were obtained and used in parameter estimation. Therefore, 12 kinetics parameters were determined with a degree of freedom of 33 (degree of freedom = No of experimental data points - No of model parameters). The following model evaluation criteria are considered:

i. All the kinetics parameters (specific reaction rates and activation energies) should be consistent with physical principles.
ii. Coefficient of determination (R^2).
iii. Lower SSR (sum of the squares of the residuals).
iv. Smaller individual confidence intervals for the model parameters.

Figure 5.2 shows the comparison between the experimental data and model predictions for the reaction scheme. The figure shows model and experimental data for naphtha, distillate, VGO, gas and coke in 390 °C, 420 °C and 450 °C. One can notice from this figure that the model predictions compared favorably with experimental data for the reactions at 390, 420 and 450 °C.

Several reactions are involved in the reaction scheme and several products are produced. During the range of contact time the model predicted higher conversion at higher temperature.

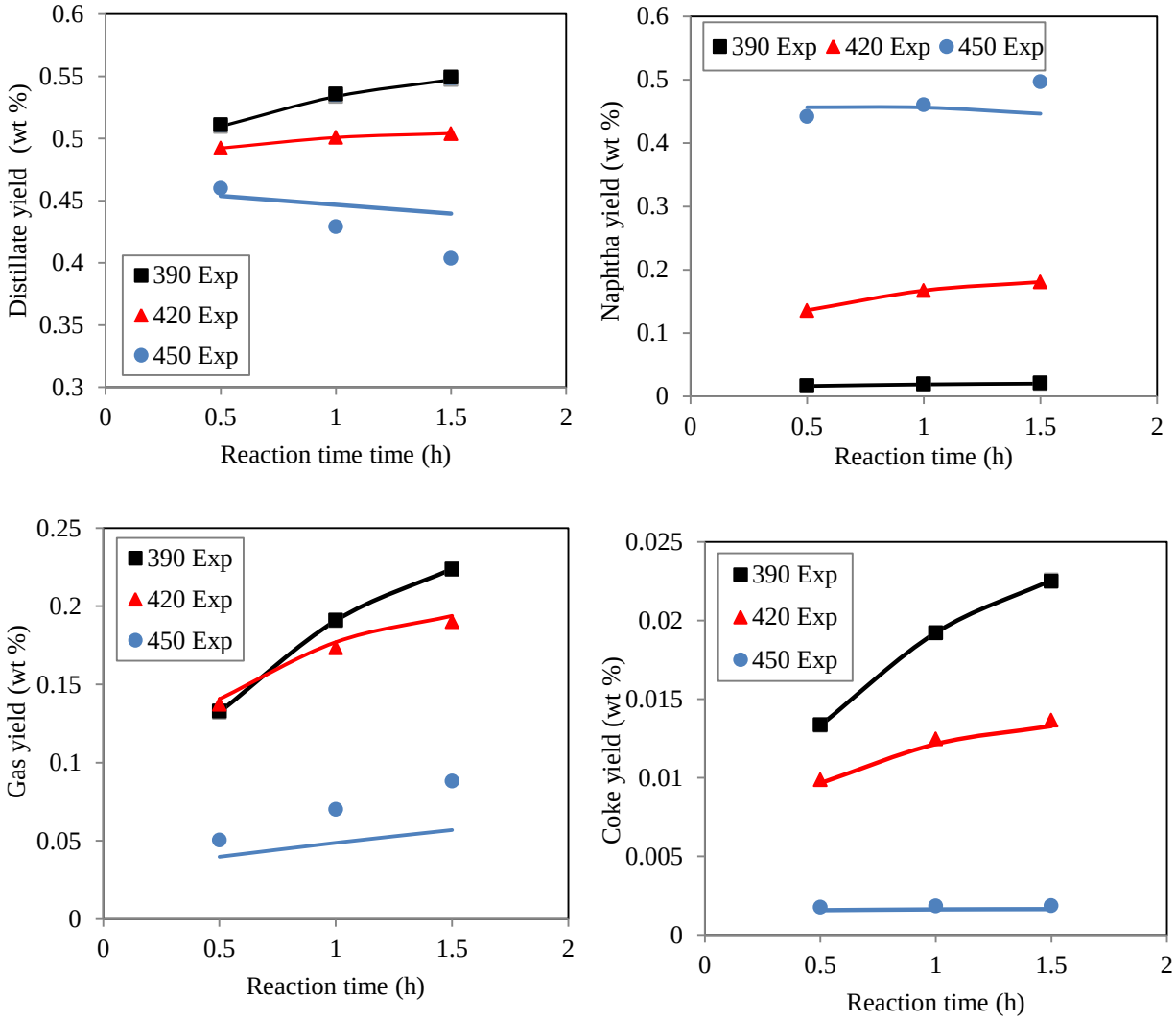


Figure 5.2: Comparison of model predicted experimental yields of naphtha, distillate, VGO, gas and coke at different reaction time and temperatures (□ 390, Δ 420, •450 °C)

The Arrhenius plots for the specific reaction rate constants are shown in Figures 5.3 and it can be observed that the figures follow the expected Arrhenius relationships, i.e., straight line with negative slope.

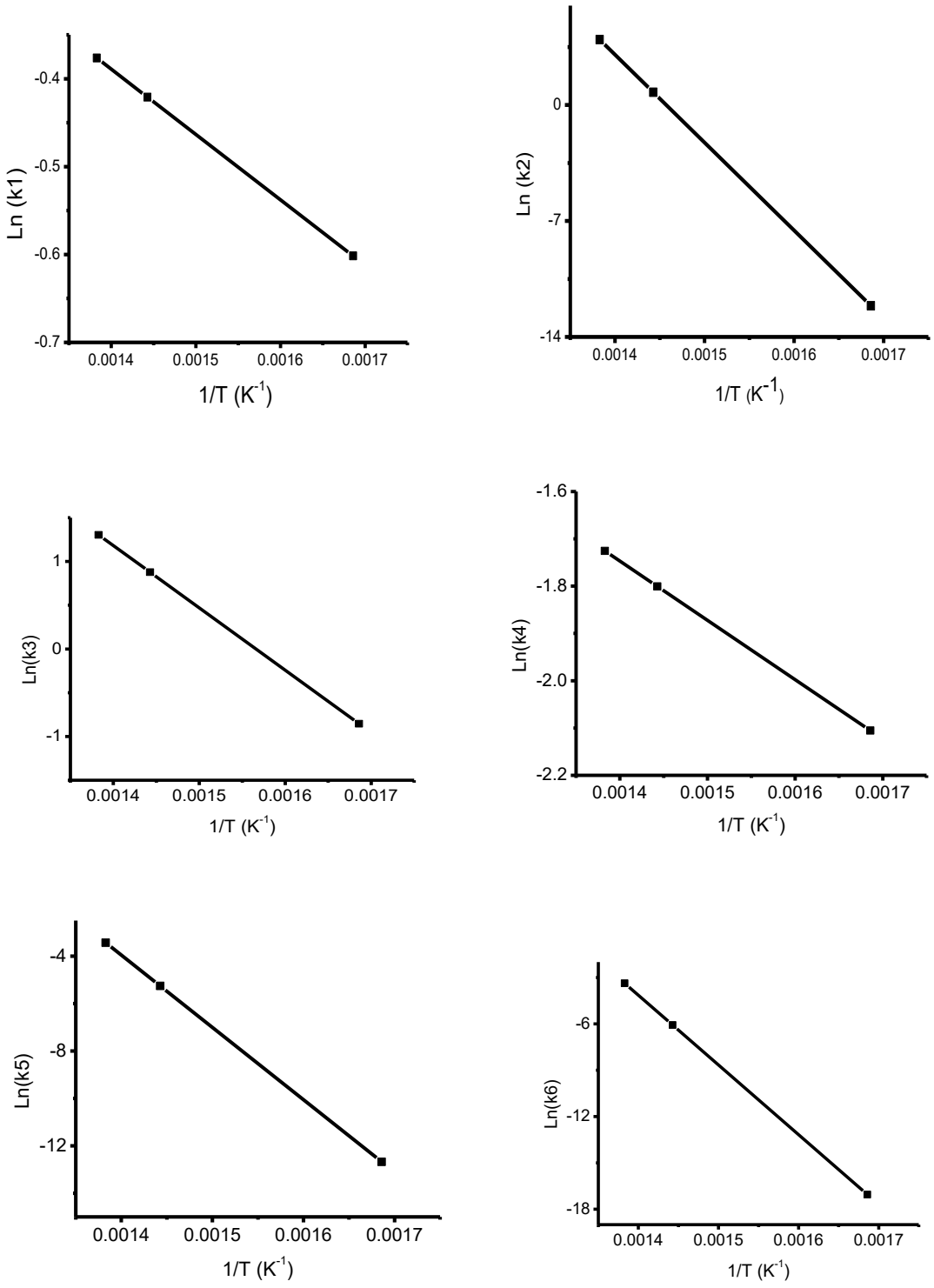


Figure 5.3: Arrhenius plots for the different specific reaction rate constants

Given all the above, it is reasonable to conclude that the proposed 5-lumped model represents the kinetics of the hydrocracking of VGO using slurry phase solid catalysts with dispersed catalysts as an additive.

Table 5.1 summarizes the estimated kinetics parameters for different reaction paths ,while Figure 5.4 shows the comparison of the specific reaction rate constants in the proposed reaction scheme. The estimated activation energy for cracking of VGO to naphtha is 105.33 kcal/mol, which is higher comparing to estimated activation energy for cracking of distillate to naphtha (60.6 kcal/mol). Therefore, the formation of naphtha will be mainly from distillate as it has the lower activation energy. Regarding the gases, the gases will be formed as the cracking of either VGO or naphtha. The estimated activation energy for cracking of VGO to gases is (14.14 kcal/mol), which is lower than cracking of naphtha to gases (89.66 kcal/mol). So the formation of gases are expected to be mainly from VGO.

Comparing the reactions in series VGO → distillate →naphtha → gases, the activation energy of VGO to distillate is the lowest (1.48 kcal/mol). The cracking of distillate to naphtha has higher activation energy (60.6 kcal/mol). While, the cracking of naphtha to gases has the highest activation energy (89.66 kcal/mol). The relative values of the estimated parameters are consistent to the product distribution.

Table 5.1: Estimated values of the parameters

Parameter	Estimated value
k_{o1}(h^{-1})	0.657
E_1 (k cal/mol)	1.477
ko_2 (h^{-1})	2.167
E_2 (k cal/mol)	105.33
ko_3 (h^{-1})	2.40
E_3 (k cal/mol)	14.14
k_{o4} (h^{-1})	0.165
E_4 (k cal/mol)	2.489
k_{o5} (h^{-1})	0.0052
E_5 (k cal/mol)	60.6
k_{o6} (h^{-1})	0.0023
E_6 (k cal/mol)	89.66

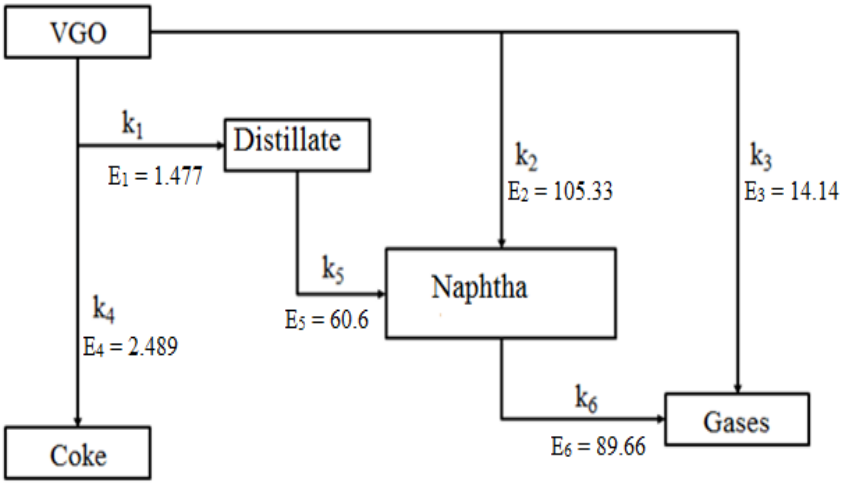


Figure 5.4: Activations Energy (kcal/mol) for different reaction pathways

Table 5.2 compares different models that were available in the open literature for hydrocracking of the VGO. It is important to mention that most of the kinetic studies on hydrocracking were conducted mainly on heavy residue and only few works are focused on the hydrocracking of VGO. Further, the reported studies considered lumping approaches using different pseudo

components. In some cases the pathways are different although the number pseudo components are same. Therefore, one should be cautious when in comparing the estimated parameters. Sadighi et al (2010) reported a 4-lumped kinetics model for hydrocracking of VGO over a zeolite based catalyst [29]. Similar to present study, they also considered VGO, distillate, naphtha and gases as the pseudo components. However, they have not taken into account of the coke formation. The activation energies for are also different due the zeolite based catalyst used by Sadighi et al (2010), while the present study used alumina based Ni-W catalyst along with a Co based dispersed catalyst. In the present study, the activation energy for gas formation is higher (59.16 kJ/mo) as reported by Sadighi et al (12.96 kJ/mol), which is possibly due to the hydrogenation effects of the dispersed catalyst. In presence of dispersed catalyst both naphtha and distillate have been increased while gas and coke formation have been decreased. Lower activation energy for distillate production (5.18 kJ/mol) also reflects the hydrogenation effects of the cracking intermediate to give stable distillate products. Sadighi et al (2010) reported a higher activation energy for distillage production (23.01 kJ/mol).

Table 5.2: Comparison of different kinetic study on Hydrocracking of VGO

Catalyst	Model	Pseudo components	Activation Energy[(a)] (kJ/mol)	Ref
Zeolite catalyst	4-lumped model	(VGO+H_2), (Distillate), (Naphtha), (Gas)	E_{VD} = 23.01 E_{VN} = 24.27 E_{VG} = 12.96 E_{DN} = 0.26 E_{DG} = 23.75 E_{NG} = 1.1E-6	[35]
Amorphous MoO_3 catalyst	6-lumped model	(VGO), (Diesel), (Kerosene), (Heavy Naphtha), (Light Naphtha)	E_{VDi} = 57.44 E_{VK} = 66.44 E_{VHN} = 125.1 E_{VLN} = 74.86 E_{DiK} = 93.40 E_{KHN} = 14.13 E_{HNG} = 16.49 E_{HNG} = 48.52	[36]
Solid catalyst (W-Ni/Al_2O_3-SiO_2) + Dispersed Catalyst (Co metal based)	5-lumped model	(VGO), (Distillate), (Naphtha), (gases), (Coke)	E_{VD} = 6.18 E_{VN} = 440.7 E_{VG} = 59.16 E_{VC} = 10.41 E_{DN} = 253.55 E_{NG} = 375.13	Present Study

(a) Activation Energies used according to different pathways available where (V=VGO), (D=distillate),(N=Naphtha),(G=gas),(C=Coke), (Di = diesel), (LN = Light Naphtha), (HN=Heavy Naphtha) and (K=Kerosine).

CHAPTER 6

CONCLUSION & RECOMMENDATIONS

6.1 Conclusions

Following are the conclusion of this experimental investigation:

i. The dispersed catalysts are effective to enhance the hydrogenation activity, which helps minimizing the coke formation.

ii. Under the studied reaction conditions (420 °C and 8 MPa), the amount of coke decreased from 2.5 wt% to less than 0.9 wt% with addition of only 500 ppm concentration of dispersed catalyst.

iii. Among the studied catalysts Co and Mo give lower amount of coke and slightly higher amount of distillate products.

iv. When supported metal catalyst used, only 0.025 C/O along with the dispersed catalyst results in conversion (51 %) that is comparable with the conversion value (54%) observed in the case of C/O of 0.1. This finding was found to be consistent with the formation of significantly lower coke production in the case of 0.025 C/O.

v. The supported and dispersed catalysts together increase the naphtha yields.

vi. The cracking VGO to distillate requires the least activation energy (1.477 kcal/mol) as compared to the other competing reactions. The estimated activation energies for cracking of VGO to naphtha is 105.33 kcal/mol and VGO to gases is 14.14 kcal/mol. Therefore, naphtha and gaseous products mainly formed via cracking of distillate, which appears by cracking of VGO.

6.2 Recommendations

i. A comprehensive study could be conducted to further investigate the kinetic of the hydrocracking reactions in a wide range of temperatures and residence time using different feeds.

ii. More investigations for the most appropriate solid catalyst could be done, in order to get a better solid catalyst with higher crushing strength and without sintering issues.

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